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## ARTICLES

# The diagonal Born–Oppenheimer correction beyond the Hartree–Fock approximation

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We report on evaluation of the diagonal Born–Oppenheimer correction (DBOC) to the electronic energy with Hartree–Fock (HF) and conventional correlated wave functions for general molecular systems. Convergence of both HF and configuration interaction (CI) DBOC with the one-particle basis seems to be rather fast, with triple- $\zeta$  quality correlation consistent sets of Dunning *et al.* sufficiently complete to approach the respective basis set limits for the DBOC of the ground state of  $\text{H}_2$  within  $0.1\text{ cm}^{-1}$ . Introduction of electron correlation via the CI singles and doubles method has a substantial effect on the absolute value of the DBOC for  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , and BH in their ground states (ca.  $+13\text{ cm}^{-1}$  out of  $115\text{ cm}^{-1}$ ,  $+22\text{ cm}^{-1}$  out of  $622\text{ cm}^{-1}$ , and  $+11\text{ cm}^{-1}$  out of  $370\text{ cm}^{-1}$ , respectively). The effect of the correlation correction to the DBOC on relative energies is small, e.g., the barrier to linearity of water changes by ca.  $1\text{ cm}^{-1}$ ; however, the value is difficult to converge to the *ab initio* limit. Based on recent results by Schwenke [J. Phys. Chem. A **105**, 2352 (2001)] and our findings, we expect the correlation correction to the DBOC to have a substantial effect on spectroscopic properties of the ground state of water. The effect of DBOC on equilibrium bond distance  $r_e$  and harmonic vibrational frequency  $\omega_e$  of the ground state of BH is  $+0.0007\text{ \AA}$  and  $-2\text{ cm}^{-1}$ , respectively. Surprisingly, the former is a much larger change than expected, and greater than errors due to residual incompleteness of electron correlation treatment and basis set in state-of-the-art conventional Born–Oppenheimer computations. The effect of using a correlated wave function for the DBOC evaluation on the above corrections to  $r_e$  and  $\omega_e$  is small. © 2003 American Institute of Physics. [DOI: 10.1063/1.1540626]

## I. INTRODUCTION

Recent advances in the single-state electron correlation problem have allowed very high accuracy solutions to the molecular nonrelativistic electronic Schrödinger equation for low-lying states of small polyatomic systems. Aside from situations where the separation of electronic and nuclear time scales is not a good approximation and the nuclear motion needs to be coupled explicitly with the electronic motion, the effect of finite nuclear time scales (non-Born–Oppenheimer) is one of the most important smaller corrections for molecules with light atoms. Problems that demand high accuracy, e.g., isotope dependence of molecular properties, high-resolution rovibrational spectroscopy, and quantum nuclear dynamics, require such effects to be taken into account quantitatively even when electronic states are well-separated and the interaction between them is small.

The approach which takes finite nuclear mass into account while preserving the time scale separation is the adiabatic approximation. The adiabatic approximation uses a product of the Born–Oppenheimer electronic wave function and a nuclear wave function as a one-term approximation to

the ground-state eigenfunction of the full molecular Hamiltonian

$$\Psi_{\text{ad}}(\mathbf{r}; \mathbf{R}) = \Psi_e(\mathbf{r}; \mathbf{R}) \Psi_n(\mathbf{R}), \quad (1)$$

where  $\mathbf{r}$  is a set of electronic coordinates and  $\mathbf{R}$  is a set of nuclear coordinates. Note the parametric dependence of the electronic wave function on nuclear positions. Although theoretical obstacles in applying the adiabatic approximation to the ground-state eigenfunction of the full nonrelativistic molecular Hamiltonian arise due to the completely continuous spectrum of the (translationally invariant) Hamiltonian,<sup>1,2</sup> ansatz (1) is the foundation of molecular structure theory and a useful practical approximation to the significantly more complicated quantitative nonadiabatic approaches.<sup>3–5</sup>

Solving for the nuclear wave function in the adiabatic approximation involves computing the adiabatic correction to the Born–Oppenheimer potential energy surface. The adiabatic correction is evaluated as

$$E_{\text{DBOC}} = \langle \Psi_e(\mathbf{r}; \mathbf{R}) | \hat{T}_n | \Psi_e(\mathbf{r}; \mathbf{R}) \rangle, \quad (2)$$

where  $\hat{T}_n$  is the nuclear kinetic energy operator. The adiabatic correction can also be considered as the first-order correction to the Born–Oppenheimer electronic energy due to the nuclear motion. Thus, it is known as the diagonal Born–

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Oppenheimer correction (DBOC; BODC abbreviation is also widely used); we will use both terms interchangeably throughout the paper.

The adiabatic correction has been evaluated accurately for up to four-electron systems;<sup>6–8</sup> however, for systems with more electrons only Hartree–Fock (HF) self-consistent field (SCF) or multiconfiguration self-consistent field (MCSCF) approximations have been used for the electronic wave functions. Evaluation of accurate adiabatic corrections for general many-electron molecular systems will be the focus of this work.

According to a recently popularized approach, the adiabatic correction is evaluated in practice as<sup>9–11</sup>

$$E_{\text{DBOC}} = \sum_I^{N_{\text{coord}}} \langle \Psi_e | -\frac{1}{2M_I} \nabla_I^2 | \Psi_e \rangle \\ = \sum_I^{N_{\text{coord}}} \frac{1}{2M_I} \left\langle \frac{\partial \Psi_e}{\partial \mathbf{R}_I} \left| \frac{\partial \Psi_e}{\partial \mathbf{R}_I} \right. \right\rangle, \quad (3)$$

where

$$\Psi_e \equiv \Psi_e(\mathbf{r}; \mathbf{R}), \quad (4)$$

and the sum is over nuclear *Cartesian* coordinates. Sellers and Pulay<sup>12</sup> used a similar expression for the adiabatic correction to derive working equations for the DBOC at the HF SCF level, although it is not clear from their paper with respect to which coordinates, internal or Cartesian, to perform differentiation. Lengsfeld and Yarkony used an analogous “Cartesian” expression to compute the off-diagonal matrix elements, i.e., bra and ket electronic wave functions in (3) corresponded to different electronic states.<sup>13</sup> Rigorous justification for the ansatz (3) evaluated in terms of Cartesian nuclear coordinates was provided by Kutzelnigg,<sup>2</sup> who referred to it as the Born–Handy ansatz.

There are two common ways to proceed with Eq. (3): use analytic gradient techniques or finite differences to evaluate the wave function derivatives. The former was particularly suitable at the HF and MCSCF levels where the familiar machinery of analytic Hessians can be used. Handy *et al.* studied the correction at the Hartree–Fock level and found the correction<sup>9</sup> and its effect on properties<sup>11</sup> to converge relatively fast with respect to the one-particle basis. The effect of the correction on the energy differences and harmonic vibrational frequencies is rather small, but non-negligible if high accuracy results are to be obtained.<sup>11</sup> The best indication of that is the recent study by Schwenke on the effects of adiabatic and nonadiabatic corrections to the ground-state potential energy surface of water on the rovibrational energy levels.<sup>14</sup> He demonstrated the importance of including both corrections to the PES and the need to go beyond the Hartree–Fock approximation to the electronic wave function for accurate adiabatic corrections. However, derivatives of general correlated wave functions are much more difficult to evaluate analytically and, to our knowledge, the DBOC has not been evaluated analytically at a correlated level. [Note, however, a recent attempt by Svrček *et al.* to

include a correlation correction to the DBOC perturbatively, rather than through explicit computation of the response of (left/right) correlated wave function.<sup>15</sup>]

The other approach to evaluating the wave function derivatives in (3) is through numerical differentiation. The advantage of the numerical method is that it is relatively straightforward to apply even to complicated wave functions.<sup>14</sup> Unfortunately, the issue of numerical stability of the wave function derivative and adiabatic correction becomes a factor. Cencek and Kutzelnigg studied the numerical approach using the explicitly correlated Gaussian geminals wave function for the hydrogen molecule.<sup>6</sup> They found that the numerical differentiation procedure was numerically stable in this case, and the standard 64-bit floating-point arithmetic was sufficient to obtain the adiabatic correction for H<sub>2</sub> accurate to 10<sup>−4</sup> cm<sup>−1</sup>. Although this conclusion may not be general, it is certainly encouraging to utilize other approximate wave functions, such as the traditional linear combinations of Slater determinants which include electron correlation indirectly to evaluate the adiabatic correction and thus to improve upon previous research in this area.

Here, we evaluate the adiabatic correction to the Born–Oppenheimer energy using conventional configuration interaction (CI) wave functions as large as full CI for a range of molecules. The goal of this study is to elucidate convergence of the adiabatic correction and related properties in the adiabatic approximation with respect to the one-particle and *N*-particle basis set completeness. The CI was chosen because it is variational, hence left- and right-hand wave functions are the same, and it is possible to approach the full CI limit straightforwardly. Coupled cluster (CC) wave functions are not nearly as convenient or flexible in this regard.<sup>16</sup>

## II. TECHNICAL DETAILS

Evaluation of the diagonal Born–Oppenheimer correction has utilized the finite-difference approximation to the wave function derivatives Eq. (3)

$$E_{\text{DBOC}} \approx \sum_I^{N_{\text{coord}}} \frac{1 - S_{\pm}}{2M_I |\delta \mathbf{R}_I|}, \quad (5)$$

where

$$S_{\pm} = \langle \Psi_{+\delta_I} | \Psi_{-\delta_I} \rangle, \quad (6)$$

$$\Psi_{\pm \delta_I} \equiv \Psi_e(\mathbf{r}; \mathbf{R}_0 \pm \delta \mathbf{R}_I). \quad (7)$$

The sum in Eq. (5) is over nuclear Cartesian coordinates, *M<sub>I</sub>* is the mass of the nucleus associated with coordinate *I*, and **R**<sub>0</sub> and **δR**<sub>*I*</sub> are the reference set of nuclear coordinates and the displacement vector corresponding to the *I*th coordinate, respectively. Hence, the evaluation of the *I*th contribution to the adiabatic correction consists of computing wave functions for plus and minus displacements and evaluating the overlap *S*<sub>±</sub> between them. Wave functions are evaluated using a determinant-based CI algorithm as implemented in the DETCI module of the PSI 3.0 electronic structure theory suite.<sup>17</sup> It is straightforward to use *strings*,<sup>18</sup> ubiquitous in determinant CI theory, to express *S*<sub>±</sub> in terms of easily computable quantities

TABLE I. Variation of the adiabatic correction with displacement size (in Bohr).

Molecule <sup>a</sup>	FP Precision	Basis set	Method	$E_{\text{DBOC}}, \text{cm}^{-1}$				
				$10^{-3}$	$5 \times 10^{-4}$	$10^{-4}$	$10^{-5}$	$10^{-6}$
H <sub>2</sub>	64	aug-cc-pVQZ	RHF	101.20	101.20	101.20	101.20	101.21
H <sub>2</sub>	128	aug-cc-pVQZ	RHF	101.20	101.20	101.20	101.20	101.16
H <sub>2</sub>	64	aug-cc-pVQZ	FCI	114.54	114.54	114.54	114.60	115.94
H <sub>2</sub>	128	aug-cc-pVQZ	FCI	114.54	114.54	114.54	114.54	114.20
H <sub>2</sub> O	64	aug-cc-pVTZ	RHF	580.09	580.12	580.13	580.13	579.81
H <sub>2</sub> O	128	aug-cc-pVTZ	RHF	580.09	580.13	580.13	580.13	580.07
H <sub>2</sub> O	64	aug-cc-pVDZ	CISD	594.66	594.69	594.70	594.72	601.37
H <sub>2</sub> O	128	aug-cc-pVDZ	CISD	594.66	594.69	594.70	594.70	594.07

<sup>a</sup>Molecular geometries for hydrogen molecule and the linear ( $D_{2h}$ ) conformer of water molecule referred to in Tables II and III.

$$S_{\pm} = \sum_{I_{\alpha}, I_{\beta}} \sum_{J_{\alpha}, J_{\beta}} C_{+\delta}(I_{\alpha}, I_{\beta}) S(I_{\alpha}, J_{\alpha}) \times S(I_{\beta}, J_{\beta}) C_{-\delta}(J_{\alpha}, J_{\beta}), \quad (8)$$

where indexes  $I$  and  $J$  label strings corresponding to the plus and minus displacements, respectively.  $S(I_{\alpha}, J_{\alpha})$  and  $S(I_{\beta}, J_{\beta})$  are overlap matrix elements between the strings. Such matrix elements are evaluated as determinants of  $N_{\alpha} \times N_{\alpha}$  and  $N_{\beta} \times N_{\beta}$  matrices, respectively, where  $N_{\alpha}$  and  $N_{\beta}$  are the number of alpha and beta electrons. The sums in Eq. (8) are restricted to include only  $(I_{\alpha}, I_{\beta})$  and  $(J_{\alpha}, J_{\beta})$  combinations allowed by the particular CI expansion. This form for  $S_{\pm}$  is applicable to closed and open-shell HF, CASSCF, RAS CI, and full CI wave functions without modification.

The optimal way to check numerical stability of the numerical differentiation is to employ higher precision arithmetic throughout the computation. Unfortunately, it would be prohibitively expensive to optimize extensive CI wave functions using 128-bit precision for general many-electron systems (e.g., H<sub>2</sub>O). To minimize the chance of any numerical problems, all wave functions were converged as tightly as technically feasible within 64-bit floating-point arithmetic.<sup>19</sup> For few-electron diatomic systems (H<sub>2</sub>, He<sub>2</sub>) highly accurate estimates of the adiabatic correction have been obtained previously<sup>6,8</sup> so we were able to check our results qualitatively against “exact” results (see the Results section). Next, we checked the influence of finite-precision round-off errors in Eq. (8) by evaluating elements of string overlap matrices (including evaluation of overlap integrals between plus and minus displaced basis functions and LU decomposition for the computation of determinants) and carrying out the summation in Eq. (8) using 64- and 128-bit precision for floating-point numbers while varying the displacement size  $\delta$  for some of the more demanding cases, i.e., those with one-particle functions of high angular momentum and/or a large number of terms in the wave function (Table I). The adiabatic correction evaluated with the single-determinant wave function changes by only a few hundredths of a  $\text{cm}^{-1}$  upon varying  $\delta$  within the  $10^{-3}$ – $10^{-5}$  a.u. range and changing floating-point precision, and thus the round-off errors are no cause for concern with RHF wave functions. The case of CI wave functions is more complicated—the loss of precision in Eq. (8) makes its evaluation unreliable when  $\delta$  is too small for the given floating-point accuracy, e.g., DBOC values ob-

tained with 128-bit floats and  $\delta=10^{-6}$  a.u. are significantly different from those obtained with smaller  $\delta$ s, and are thus considered unreliable. Breakdown of numerical stability is even more pronounced when 64-bit arithmetic is used. However, the displacement size of  $5 \times 10^{-4}$  a.u., as recommended by Cencek and Kutzelnigg,<sup>6</sup> seems to be a good choice with conventional CI wave functions, and henceforth we adopted it for all computations. Since for our purposes the use of 128-bit floating-point arithmetic, as described above, increases computation time insignificantly in the majority of cases, we decided to perform all production computations in such a way. Furthermore, although the numerical differentiation approach for DBOC may become unsuitable in cases where very extensive expansions with high-order angular dependence are used, in all our examples the error due to incompleteness of the one-particle basis set and correlation treatment are significantly larger than the anticipated error in the result due to numerical errors and presence of  $O(\delta^3)$  and higher terms in the numerical wave function derivative.

We used the following Gaussian basis sets: DZ,<sup>20</sup> DZP,<sup>20</sup> cc-pVXZ,<sup>21,22</sup> and aug-cc-pVXZ.<sup>21–23</sup> Basis sets were obtained from the extensible computational chemistry environment basis set database.<sup>24</sup> Pure spherical harmonic Gaussians were used throughout, except with the DZP basis set. All computations were performed in  $C_1$  symmetry for simplicity, e.g., to avoid rotating wave functions from the point group’s canonical frame of coordinates back to the laboratory frame. The  $1s$ -like orbital was kept doubly occupied in correlated computations on BH and H<sub>2</sub>O, unless noted otherwise.

The following conversion factors have been employed:  $1 E_h = 219\,474.631\,371\,0 \text{ cm}^{-1}$ ,  $m_e = 5.485\,799\,110 \times 10^{-4}$  a.m.u.,  $1 \text{ bohr} = 0.529\,177\,249 \text{ \AA}$  (1998 CODATA recommended values). Nuclear masses used to evaluate DBOC were derived from atomic masses published in the online NIST database of atomic weights<sup>25</sup> by subtracting the mass of electrons. Atomic masses were used to evaluate harmonic vibrational frequencies.

### III. RESULTS

#### A. Ground state of H<sub>2</sub>

The adiabatic correction for the hydrogen molecule in its electronic ground state is presented in Table II. Convergence



TABLE II. Adiabatic correction for the ground electronic state of  $H_2$  at  $r_{HH}=1.4$  a.u. (in  $cm^{-1}$ ).

Basis	RHF	FCI
cc-pVDZ	99.425	111.95
cc-pVTZ	101.110	114.66
cc-pVQZ	101.257	114.62
cc-pV5Z	101.275	114.63
cc-pV6Z	101.265	114.61
aug-cc-pVDZ	98.131	111.25
aug-cc-pVTZ	100.963	114.45
aug-cc-pVQZ	101.202	114.54
aug-cc-pV5Z	101.247	114.59
aug-cc-pV6Z	101.252	...
Complete	101.259 <sup>a</sup>	114.591 <sup>b</sup>

<sup>a</sup>Obtained by fitting aug-cc-pV(T,Q,5,6)Z RHF adiabatic corrections to  $E_X = E_\infty + a \exp(-bX)$ .

<sup>b</sup>Reference 6.

of the adiabatic correction computed with the Hartree–Fock wave function is rather fast (see Table II). Triple- $\zeta$  quality basis sets with polarization functions are sufficient to compute the DBOC with an absolute error of  $\sim 0.3$   $cm^{-1}$ . Addition of diffuse functions to the basis (aug-cc-pVXZ labeled sets) seems to decrease the rate of convergence slightly, e.g., the RHF/cc-pVTZ DBOC is only  $0.15$   $cm^{-1}$  away from the basis set limit, while the error in the aug-cc-pVTZ value is twice as large, about  $0.30$   $cm^{-1}$ . This is certainly unexpected. Chances are very slim that this is due to numerical round-off errors since we did not find any indication for such numerical problems (see Numerical Details). Note that RHF/cc-pVXZ DBOC values converge nonmonotonically to the estimated basis set limit, unlike the RHF/aug-cc-pVXZ data. This behavior is echoed by the corresponding FCI values as well.

The RHF DBOC values are in error by ca.  $13$   $cm^{-1}$  due to the lack of electron correlation in the wave function. All highly accurate adiabatic corrections for the ground-state PES of  $H_2$  to date have been computed utilizing explicitly correlated wave functions of Gaussian geminals.<sup>26–28</sup> Most recently, Cencek and Kutzelnigg have established DBOC estimates converged in a wide range of internuclear distances to  $10^{-4}$   $cm^{-1}$  by employing a 1200-term expansion.<sup>6</sup> The utmost accuracy of the wave function, and, subsequently, the BO energy and adiabatic correction, is due to its explicit dependence on the interelectronic distance  $r_{12}$ . Conventional CI wave functions generated from a finite one-particle space cannot attain the same level of accuracy due to their lack of an electron–electron cusp. This reflects in slow asymptotic convergence of such wave functions and corresponding energies with respect to the one-particle basis set. Thus, one would expect slow convergence of the adiabatic correction evaluated at the CI level with respect to the number of terms in the wave function.

Convergence of the FCI DBOC with respect to the cardinal number of the correlation-consistent basis set family is similar to that of RHF DBOC, e.g., the error in FCI DBOC computed with the aug-cc-pVQZ basis is ca.  $0.04$   $cm^{-1}$  versus a ca.  $0.05$   $cm^{-1}$  basis set incompleteness error at the RHF/aug-cc-pVQZ level. This is rather surprising consider-

ing how slow the asymptotic convergence of the correlation energy is compared to that of the Hartree–Fock electronic energy.<sup>29,30</sup> FCI/aug-cc-pVXZ adiabatic corrections converge monotonically from below, similarly to DBOC computed by Cencek and Kutzelnigg with explicitly correlated Gaussian wave functions, and in contrast with the FCI/cc-pVXZ counterparts.

However, if one looks at convergence of DBOC as a function of the number of terms in the wave function expansion, it is much slower compared to the case of explicitly correlated wave functions. For example, the FCI/aug-cc-pVQZ expansion has 1256 symmetry-unique terms in  $D_{2h}$  symmetry, but is still in error by ca.  $0.05$   $cm^{-1}$ . That is about an order of magnitude less accurate than the value obtained with Cencek and Kutzelnigg’s explicitly correlated wave function with only 150 terms.<sup>6</sup>

Despite the lower accuracy of the adiabatic correction obtained with conventional CI wave functions compared to that of previously computed values of DBOC, it is encouraging to see that absolute accuracy of  $0.1$   $cm^{-1}$  can be achieved with triple- $\zeta$  quality correlation-consistent basis sets.

## B. Ground state of $H_2O$

Water was one of the first “heavy” polyatomic molecules for which the adiabatic correction has been evaluated. Bardo and Wolfsberg computed the DBOC for the ground state to be  $600$   $cm^{-1}$  at the RHF/DZP level.<sup>31</sup> Handy *et al.* concluded that their RHF/TZ2P value of  $595$   $cm^{-1}$  was within  $5$   $cm^{-1}$  of the Hartree–Fock limit.<sup>9</sup> Recent attempts have aimed to correct the ground-state potential energy surface (PES) of water in order to predict its rovibrational spectrum. Zobov *et al.* computed the adiabatic correction surface at the RHF level and concluded that adiabatic effects were not as important for accurate predictions of rovibrational eigenvalues as nonadiabatic effects.<sup>32</sup> Since then, Schwenke has evaluated not only an adiabatic correction surface at the CASSCF level but also the second-order, nonadiabatic correction.<sup>14</sup> He observed much stronger effect of the adiabatic correction relative to the nonadiabatic correction on pure bending vibrational levels, whereas the nonadiabatic effects were somewhat more important of the two for stretching and mixed vibrational eigenstates. Schwenke’s treatment of the DBOC was superior to previous studies as the wave function included some amount of electron correlation. The inclusion of electron correlation seems important for describing low-lying stretching vibrations in the molecule, as the effect of the CASSCF DBOC on those levels differed from that of the RHF DBOC by as much as  $1.17$   $cm^{-1}$  and was comparable to the effect of the nonadiabatic correction. However, the quality of the electronic wave function is still too limited to make definite conclusions as to what level of theory is sufficient to compute the adiabatic correction in water with a prescribed accuracy. The importance of water as a benchmark test for theoretical spectroscopy and as a prototypical polyatomic system with complicated electronic structure prompted us to investigate the convergence of the DBOC with level of theory in more detail. To our knowledge

TABLE III. Adiabatic correction to the barrier to linearity of water in the ground state (in  $\text{cm}^{-1}$ ).

Basis	Method	$C_{2v}$ <sup>a</sup>	$D_{\infty h}$ <sup>a</sup>	$\Delta E_e$ <sup>b</sup>
DZ	RHF	613.66	587.69	-25.97
DZ	CISD	622.40	596.43	-25.97
DZ	CISDT	623.62	597.56	-26.06
DZ	CISDTQ	624.56	598.28	-26.28
DZ	CISDTQP	624.61	598.32	-26.29
DZP	RHF	597.88	581.32	-16.56
cc-pVDZ	RHF	600.28	585.20	-15.08
cc-pVDZ	CISD (ae) <sup>c</sup>	615.62	599.75	-15.87
cc-pVDZ	CISD	615.03	599.15	-15.88
cc-pVDZ	CISDT	616.82	600.62	-16.20
cc-pCVDZ	RHF	599.92	584.54	-15.38
cc-pCVDZ	CISD (ae) <sup>c</sup>	621.52	605.47	-16.05
cc-pCVDZ	CISD	615.03	598.93	-16.10
cc-pVTZ	RHF	596.53	581.43	-15.10
cc-pVTZ	CISD (ae) <sup>c</sup>	613.48	598.40	-15.08
cc-pVTZ	CISD	611.89	596.73	-15.16
cc-pVQZ	RHF	595.57	580.72	-14.85
aug-cc-pVDZ	RHF	594.93	580.77	-14.16
aug-cc-pVDZ	CISD	608.68	594.69	-13.99
aug-cc-pV(T/D)Z <sup>d</sup>	RHF	593.71	579.53	-14.18
aug-cc-pV(T/D)Z <sup>d</sup>	CISD	607.85	594.12	-13.73
aug-cc-pVTZ	RHF	594.61	580.13	-14.48
aug-cc-pVQZ	RHF	594.89	580.32	-14.57

<sup>a</sup>Geometries from Ref. 31.<sup>b</sup>The difference between the adiabatic correction for  $D_{\infty h}$  and  $C_{2v}$  structures.<sup>c</sup>All electrons were correlated.<sup>d</sup>aug-cc-pVTZ set on O, aug-cc-pVDZ set on H.

the adiabatic correction has never been computed for a system with more than four electrons with wave functions as extended as we use here.

We chose to compute the adiabatic correction at two stationary points on the PES of water: the equilibrium  $C_{2v}$  and the linear  $D_{\infty h}$  structure at the geometries utilized in Refs. 33 and 34. The goal is to study convergence of the adiabatic correction in absolute and relative contexts with respect to the one-particle basis and correlation treatment. Furthermore, the energy difference between the two, the barrier to linearity of water, has been the subject of considerable theoretical scrutiny in recent years,<sup>33–35</sup> not the least due to its importance as one of the key characteristics of the PES.<sup>36</sup> The highly accurate *ab initio* estimates of the barrier have relied on a single value for the DBOC compared with a RHF/DZP wave function ( $-17 \text{ cm}^{-1}$ ). A converged value for the DBOC contribution to the barrier would reduce the remaining uncertainty in the *ab initio* value for the barrier, currently standing at  $11\,119 \pm 15 \text{ cm}^{-1}$ .<sup>34</sup> We hope to expand our treatment of the ground-state surface for  $\text{H}_2\text{O}$  to include more nuclear configurations in the future.

The adiabatic correction for the two structures of water is presented in Table III. The first observation is that an aug-cc-pVDZ or cc-pVTZ basis set is sufficient to obtain the RHF DBOC with an absolute accuracy of  $1 \text{ cm}^{-1}$ . The RHF/aug-cc-pVXZ series seems to converge very well, better than the RHF/cc-pVXZ one. The basis set limits for the RHF DBOC estimated by the aug-cc-pVQZ RHF DBOC value are ca.  $594.9$  and  $580.3 \text{ cm}^{-1}$  for  $C_{2v}$  and  $D_{\infty h}$  structures, respectively.

Inclusion of electron correlation has a significant effect on the absolute value of DBOC. Let us consider, for example, the  $C_{2v}$  structure. The effect of including up to quintuple valence excitations with the DZ basis is ca.  $10.9 \text{ cm}^{-1}$ ,  $8.7 \text{ cm}^{-1}$  of which is accounted for at the singles and doubles level. The correlation contribution to the DBOC grows as the basis set is expanded—with the cc-pVDZ basis the correlation contribution from singles and doubles is  $14.7 \text{ cm}^{-1}$ , with triple excitations contributing another  $1.8 \text{ cm}^{-1}$ . The effect of electron correlation on the relative DBOC is of course smaller: it's ca.  $+0.7 \text{ cm}^{-1}$  at the CISD/cc-pVDZ level and increases to ca.  $+1.1 \text{ cm}^{-1}$  upon inclusion of triple excitations. With the larger cc-pVTZ basis the correlation contribution to the relative DBOC is virtually zero, but addition of diffuse basis functions yields a relative contribution of  $-0.2 \text{ cm}^{-1}$  at the CISD/aug-cc-pVDZ level. Thus, while the absolute effect of electron correlation is rather large and converges monotonically, its effect on the DBOC contribution to the relative energy is rather small but difficult to converge. Our best estimate for the DBOC contribution to the barrier to linearity is  $-14 \pm 1 \text{ cm}^{-1}$ , or  $3 \text{ cm}^{-1}$  higher than the previous prediction.<sup>33</sup> The revised value for the DBOC contribution thus increases the current best *ab initio* estimate of the barrier to linearity of water to  $11\,122 \pm 13 \text{ cm}^{-1}$ .

Other effects of interest are that of correlating electrons in the  $1s$ -like orbital. Core correlation brings about rather significant change to the absolute DBOC value, about  $+1.6 \text{ cm}^{-1}$  at the CISD/cc-pVTZ level, and, dramatically larger, a ca.  $+6.5 \text{ cm}^{-1}$  effect at the CISD/cc-pCVDZ level, when the core region of the basis set is properly equipped with high exponent functions. However, core correlations seems to affect the relative DBOC very little, by less than  $0.1 \text{ cm}^{-1}$ ; hence, we expect this effect to be of much lower importance than the contribution to DBOC from valence correlation across the potential energy surface of water.

It is clear that the effect of electron correlation on the absolute value of the DBOC is rather significant,  $21$ – $22 \text{ cm}^{-1}$  with the CISD(ae)/cc-pCVDZ wave function. It is difficult to extrapolate from our results for the barrier to linearity of how important the effect of the DBOC is on relative energies since the correlation contribution to the barrier is probably less than  $1 \text{ cm}^{-1}$ . However, recent studies of vibrational energy levels of water indicate that it is critical to move beyond the Hartree–Fock approximation to describe the effect of adiabatic correction on rovibrational energy levels at the  $1 \text{ cm}^{-1}$  accuracy threshold.<sup>14,37</sup> Furthermore, the CASSCF/cc-pVTZ DBOC correction surface by Schwenke is about  $8 \text{ cm}^{-1}$  higher than its RHF/aug-cc-pVTZ analog at the vibrationally averaged nuclear configuration,<sup>14</sup> whereas our results indicate that the effect of valence correlation on the DBOC is about twice that amount. Therefore, we conclude that future studies that compute the adiabatic correction with high accuracy should employ wave functions with enough flexibility to describe electron correlation, either directly as done here, or, possibly, indirectly through the use of natural orbitals.<sup>38</sup>

TABLE IV. Effect of the adiabatic correction on the equilibrium bond distance and quadratic force constant for the ground electronic state of BH.  $r_e$  (in Å) and  $f''$  (in aJ Å<sup>-2</sup>) were determined by fitting a fourth-order polynomial to a set of five energies evaluated at bond distances displaced by (-0.01 Å, -0.005 Å, 0.0 Å, 0.005 Å, 0.01 Å) about 1.235 39 Å.  $\omega_e$  are reported in cm<sup>-1</sup>.

	Born–Oppenheimer <sup>a</sup>	Adiabatic	
		+RHF DBOC <sup>b</sup>	+CISD DBOC <sup>c</sup>
$r_e$	1.235 39	1.236 00	1.236 05
$f''(r_e)$	3.001 3	2.996 0	2.995 5
$f'^{BO}(r_e)^d$	3.001 3	2.991 8	2.990 9
$f''(r_e^{BO})^e$	3.001 3	3.005 4	3.005 9
$\omega_e^f$	2348.85	2346.77	2346.61
$E_{\text{DBOC}}^g$	...	359.25	369.97

<sup>a</sup>Energy evaluated at CCSD(T)/aug-cc-pVTZ level of theory.

<sup>b</sup>The Born–Oppenheimer energy+aug-cc-pVTZ RHF DBOC.

<sup>c</sup>The Born–Oppenheimer energy+aug-cc-pVTZ CISD DBOC.

<sup>d</sup>Born–Oppenheimer quadratic force constant evaluated at  $r_e$ .

<sup>e</sup>Quadratic force constant evaluated at Born–Oppenheimer  $r_e$ .

<sup>f</sup>Evaluated at  $r_e$  using atomic masses.

<sup>g</sup>The DBOC (in cm<sup>-1</sup>) evaluated at  $r = 1.235\,39$  Å.

### C. Ground state of BH

Boron hydride is a standard benchmark for *ab initio* quantum chemistry due to its “only” six electrons. One would expect that a very high accuracy theoretical description could be attained for such a small molecule. Nevertheless, the effect of the adiabatic correction on its properties is not known. Comparison to an accurate Born–Oppenheimer estimate for the equilibrium geometry  $r_e$ , due to Martin, with the experimental value reveals a large discrepancy of about 0.0025 Å.<sup>39</sup> The authors attributed the difference to the nonadiabatic effect and assumed the influence of the adiabatic correction to be negligible. Handy *et al.* have shown that the effect of the Hartree–Fock DBOC on equilibrium bond distances of small first-row diatomics is indeed much smaller than 0.0025 Å.<sup>11</sup> However, its effect on harmonic vibrational frequencies is sizable and for H<sub>2</sub> is more important than that of using atomic rather than nuclear masses, which accounts indirectly for nonadiabatic correction.<sup>11</sup> Martin found that the “best” Born–Oppenheimer harmonic vibrational frequency for the ground state of BH is in error by ca. 1.3 cm<sup>-1</sup>,<sup>39</sup> a discrepancy that could be rectified by incorporating the adiabatic correction. Hence, we decided to investigate the effect of the adiabatic correction on  $r_e$  and  $\omega_e$  of the ground state of BH since accurate data are not available at this point. The results are presented in Table IV. As a reference Born–Oppenheimer electronic structure method, we used CCSD(T)/aug-cc-pVTZ. Properties computed at this level are in substantial error, but the goal of this study was only to evaluate the magnitude of the effect of DBOC on the equilibrium properties and not to make final predictions thereof in the adiabatic approximation. To achieve the latter goal, we would need to use an *ab initio* limit Born–Oppenheimer potential in the relativistic limit. Work along these lines is in progress.

Let us first note the significant effect of the adiabatic correction on  $r_e$ , ca. +0.0007 Å. It is certainly not negligible in this case, e.g., it is much larger than the FCI correc-

tion of +0.0002 Å, defined as the  $r_e(\text{FCI/cc-pVTZ}) - r_e(\text{CCSD(T)/cc-pVTZ})$  difference, and the  $r_e(\text{CCSD(T)/cc-pV6Z}) - r_e(\text{CCSD(T)/cc-pV5Z})$  difference of -0.000 12 Å, both listed in Table 4 of Ref. 39. The large effect on  $r_e$  goes against the trend observed by Handy and Lee for ground states of light diatomics.<sup>11</sup> To recap their findings, the effect of the RHF/6-31G\* DBOC on equilibrium bond distances decreased sharply along the series H<sub>2</sub>→HF→N<sub>2</sub>→F<sub>2</sub>. The largest effect was observed in the case of the hydrogen molecule, ca. 0.0002 Å, or about one-third of the effect we observe for BH. In comparison, for hydrogen fluoride the effect was an order of magnitude smaller, only ca. 0.000 02 Å.<sup>11</sup> Thus, the large effect of the DBOC on  $r_e$  for boron hydride is rather surprising. A more systematic study is warranted to study the effect of the adiabatic correction on  $r_e$  in first-row diatomic hydrides at correlated levels of theory.

The effect of the adiabatic correction on the quadratic force constant is also substantial, about -0.0068 aJ Å<sup>-2</sup>. We separate the change in  $f''$  into two components, the direct contribution of the DBOC and an indirect effect due to the dependence of the second-order force constant on the internuclear separation.<sup>40</sup> The direct effect increases the force constant, and the indirect effect is about twice the magnitude of the former and of opposite sign. The resulting effect of the DBOC on the harmonic vibrational frequency is substantial, about -2 cm<sup>-1</sup>. This effect is larger than the discrepancy of 1.3 cm<sup>-1</sup> between the best “Born–Oppenheimer” result<sup>39</sup> and the experimentally derived  $\omega_e$ ,<sup>41</sup> but adjusts the frequency in the right direction.

The effect of electron correlation in the electronic wave function used to evaluate the DBOC has a rather small effect on  $r_e$  and  $\omega_e$ , although not completely negligible for  $r_e$ . We do not expect to see significant changes upon expansion of the  $N$ -particle space beyond CISD, at least in the case of the ground state of BH.

### IV. SUMMARY

We report on evaluation of the adiabatic correction to the Born–Oppenheimer electronic energies with Hartree–Fock and conventional correlated wave functions for general molecular systems. Evaluation of a finite-difference expression for the DBOC was found to be sufficiently stable numerically to perform computations with the standard IEEE 64-bit floating-point computer arithmetic. Convergence of both HF and CI DBOC with the one-particle basis seems to be rather fast, with triple- $\zeta$  quality correlation consistent sets of Dunning *et al.* sufficiently complete to approach the respective basis set limits for the DBOC of the ground state of H<sub>2</sub> within 0.1 cm<sup>-1</sup>.

Introduction of electron correlation via the CI singles and doubles method has a substantial effect on the absolute value of the DBOC for H<sub>2</sub>, H<sub>2</sub>O, and BH in their electronic ground states (ca. +13 cm<sup>-1</sup> out of 115 cm<sup>-1</sup>, +22 cm<sup>-1</sup> out of 622 cm<sup>-1</sup>, and +11 cm<sup>-1</sup> out of 370 cm<sup>-1</sup>, respectively). The effect of the correlation correction to the DBOC on relative energies is small, e.g., the barrier to linearity of water changes by ca. 1 cm<sup>-1</sup>; however, the value is difficult to converge. Based on recent results by Schwenke and our find-



ings, we expect the correlation correction to the DBOC to have a substantial effect on vibrational band origins of the electronic ground state of water.

The effect of the adiabatic correction on equilibrium bond distance,  $r_e$ , and harmonic vibrational frequency,  $\omega_e$ , of the ground state of BH is  $+0.0006 \text{ \AA}$  and  $-2 \text{ cm}^{-1}$ , respectively. Surprisingly, the former is a much larger change than expected, and more significant than errors due to residual incompleteness of electron correlation treatment and basis set in state-of-the-art conventional Born–Oppenheimer computations.<sup>39</sup> Using correlated wave function for the DBOC changes the above corrections to  $r_e$  and  $\omega_e$  insignificantly.

The primary conclusion of the study is that it is necessary to use correlated wave functions to evaluate the adiabatic correction if high accuracy spectroscopic properties are sought.

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